

V.D.10 Silane Activation by Transition Metal Catalysts for Hydrogen Storage

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hydrogen fuel produced, rate of production, and its thermodynamics (or heat of reaction).

Abstract

We describe the application of oxo and imido rhenium complexes in the production of molecular hydrogen (H_2) from the catalytic hydrolysis and alcoholysis of organosilanes. The main highlights of the reaction are quantitative hydrogen yields of 99% purity, low catalyst loading (0.10 mol%), ambient conditions, and no solvent requirement. The amount of hydrogen produced is proportional to the water or alcohol stoichiometry. Thus, reaction mixtures of polysilyl organics such as $HC(SiH_3)_3$ contain >6% by weight hydrogen. We developed a single-quadrupole mass spectrometer interfaced with a vacuum system for measuring the kinetics of H_2 evolution in real time. Kinetic and isotope labeling experiments have revealed a new mechanistic paradigm for the activation of Si-H bonds by high-valent oxo and imido catalysts.

We have synthesized and are exploring organometallic catalysts for hydrogen production via dehydrocoupling of organosilanes that are hydrogen rich, analogs of hydrocarbons. The resulting polysilanes are easily re-hydrogenated catalytically with dihydrogen over rhodium catalysts.

Objectives

Investigate the kinetics and mechanisms of hydrogen evolution from the reaction of organosilanes with water or alcohols as catalyzed by oxo and imido complexes of rhenium. Determine the rate determining elementary steps and physical factors that govern their kinetics. Develop new catalyst systems for the production of hydrogen from dehydrocoupling of organosilanes and investigate catalytic regeneration of Si-H bonds using dihydrogen.

Technical Barriers

One of the two challenges facing the implementation of a "hydrogen economy" is the ability to store enough fuel (preferably in liquid form) on-board for vehicular application. A catalytic system is a desirable approach for controlling the kinetics of hydrogen release for use in fuel cells. Among the important challenges to be addressed are hydrogen density content, volumetric content, purity of the

Progress Report and Future Directions

We have developed efficient, readily accessible, and high yielding (70-90% overall) syntheses for cationic oxo and imido rhenium complexes of oxazoline and salen ligands (Figure 1). While high-valent metal complexes are ubiquitous in oxidations, we have shown that oxo

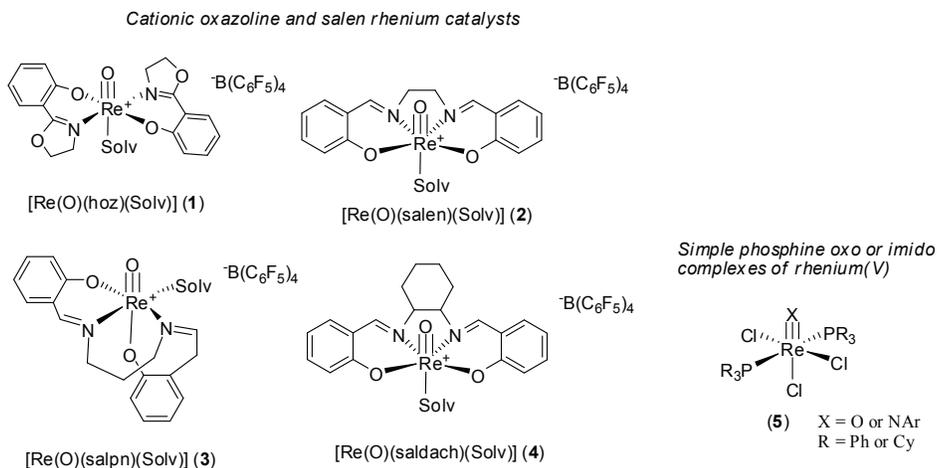


FIGURE 1. Oxo and Imido Rhenium Catalysts for Hydrolytic and Alcoholic Dehydrogenation of Silanes

and imido complexes of rhenium(V), as those in Figure 1, catalyze the hydrolysis and alcoholysis of Si-H bonds under ambient conditions (Figure 2). Furthermore, we discovered that even simple oxo and imido phosphine complexes of rhenium(V), albeit less reactive than their cationic coordination analogs, affect hydrogen release from mixtures of organosilane and alcohols.

Reaction rates of gas evolution are often measured by volume displacement or by employing pressure transducers, which have several limitations. Neither method provides identification of products. Measuring pressure change can be done properly only over a narrow dynamic range as maintaining a constant temperature becomes more difficult per $PV = nRT$. The price of a minimal commercial mass spectrometry system (> \$50K) is somewhat prohibitive for a single laboratory. Therefore, we have developed a new mass spectrometer (instrument) that uses commercially available components for approximately \$24K. An RGA single quadrupole mass spectrometer was installed in a small vacuum system with a differentially pumped inlet, allowing real-time monitoring of reactants and/or products from reaction systems near atmospheric pressure. An added benefit is that we are able to perform isotope analyses in real time. The mass spectrometer is a universal detector, and analysis is rapid and very sensitive. A picture of the setup is shown in Figure 3.

We have characterized the kinetics in detail for two catalysts, $[\text{Re}(\text{O})(\text{hoz})_2(\text{Solv})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) and $\text{Re}(\text{X})\text{Cl}_3(\text{PPh}_3)_2$ (**5**), where $\text{X} = \text{O}$ or NAr . The rate law for **1** is first-order in $[\text{Re}]$ and organosilane but zero-order in water and alcohol. Isotope-labeling experiments showed that molecular hydrogen in the product is made of one hydrogen atom from

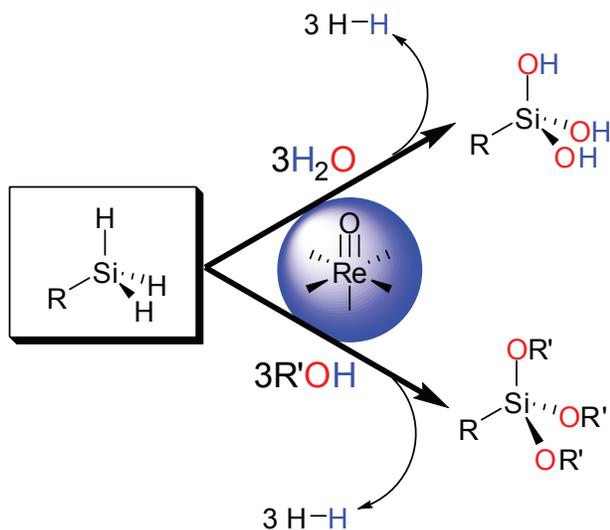


FIGURE 2. Reactions of Organosilane with Water and Alcohol Catalyzed by High-Valent Rhenium

organosilane and the other from water or alcohol. The silanol contains exclusively oxygen from water even under stoichiometric conditions. A primary kinetic isotope effect of 1.4 is observed for Si-H versus Si-D, and no kinetic isotope effect is observed for D_2O or ROD. The solvent open coordination site is required for catalysis. These results are in agreement with a mechanism in which the silane coordinates to rhenium in the rate-determining step.

The reaction of **5** with Et_3SiH produced the hydride $\text{Re}(\text{O})(\text{H})\text{Cl}_2(\text{PPh}_3)_2$. Stoichiometric kinetics featured first-order in **[5]** and $[\text{Et}_3\text{SiH}]$, and rate inhibition by $[\text{PPh}_3]$. However, the rhenium hydride was not very reactive towards alcohols or water. It required acid to liberate H_2 . Furthermore, when the rate constants obtained under stoichiometric conditions were used to simulate steady-state kinetics, they failed to demonstrate the observed reactivity under catalytic conditions. Nevertheless, steady-state kinetics showed that association of **5** with silane is rate-determining, and we have hypothesized a concerted ionic mechanism to account for all experimental observations.

One major drawback of the hydrolysis and alcoholysis of organosilanes is the production of silanols and silyl ethers, respectively. Both products contain thermodynamically robust Si-O bonds, which require reactive (and expensive) hydrides to recycle back to the organosilane fuel. Therefore, we have begun studying organometallic catalysts for dehydrocoupling of hydrogen-rich organosilanes, analogs of hydrocarbons, Figure 4. Thus far the best catalysts in hand dehydrogenate only 1-2 of the available hydrogen equivalents on the silane giving low molecular weight polysilanes. We plan on investigating the kinetics and mechanisms of these reactions to understand which properties on the catalyst are desirable. We will also be investigating the regeneration of Si-H bonds via catalytic



FIGURE 3. In-House Built for Measuring Kinetics and Purity of H_2 Evolution in Real Time

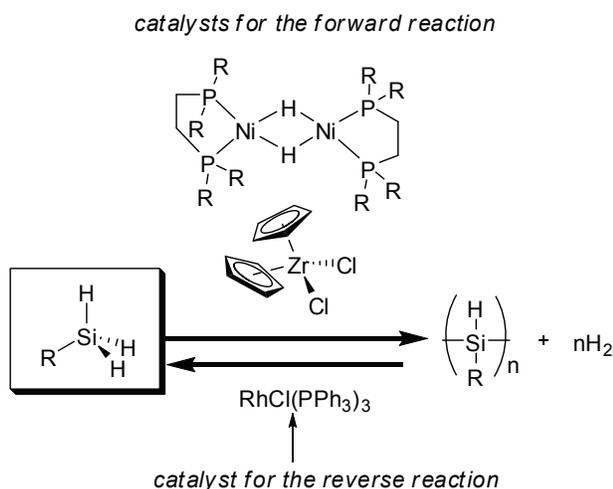


FIGURE 4. Dehydrocoupling of Silanes Using Organometallic Catalysis

hydrogenation of polysilanes. The zirconium catalysts require activators such as $\text{Al}(\text{CH}_3)_3$ and MeLi . We will explore the activator effect on the kinetics, conditions, and hydrogen yields.

Publications (Including Patents) Acknowledging the Grant or Contract

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